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Thermal Oxidation and Hydrolytic Stability of Polymers with Main Inorganic Molecular Chains [x)]

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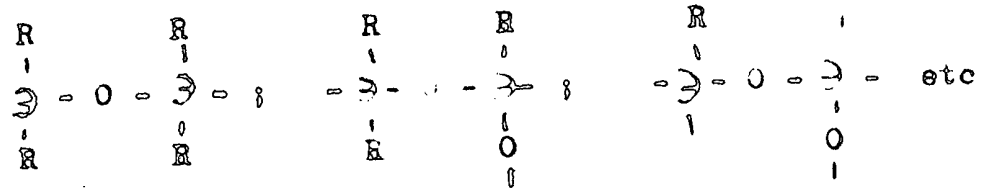
Thermal oxidation and hydrolytic stability of polymers is determined by the chemical composition and structure of molecules. There are many investigations concerning the thermal oxidation stability of organic polymers (1-4), some representative polyorganosiloxanes having also been dealt with (5-6).

The structure of main inorganic molecular chains of a considerable number of polymers known at present can be vizualised in terms of the following types:



The main chains are formed by different chemical elements such as silicon, titanium, tin, aluminium, boron, as well as their combinations and are usually fringed with organic, organosiloxane and other groups.

The study of polymers with inorganic molecular chains is of a definite interest. In this communication it will be attempted to compare the thermal oxidation destruction of some classes of organic polymers and that of polymers with main inorganic molecular chains, as well as to consider the effect

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x) Translated by A.Pumpiansky, Moscow

of the structure and chemical composition of the latter on their thermal oxidation and hydrolytic stability. The thermal oxidation destruction was usually, but not always determined on pure polymers without any fillers and estimated in terms of the loss in the weight of the polymer heated at different temperatures in the presence of atmospheric oxygen, the magnitude of thermoplasticity of polymeric films on metallic supports and finally, the change in chemical composition.

To estimate the thermal oxidation stability by the change in the weight of the polymer on heating use was made of organic polymers of different chemical composition and polymers with main inorganic chain molecules fringed with various organic groups. Experimental data listed in Table 1 indicate the change in weight of different polymers when heated at 250, 300, 350, 400, and 450° for 24 hours.

As seen from the Table the thermal oxidation stability of organic polymers is distinctly different from that of polymers with inorganic molecular chains, the organic polymers losing considerably more weight after being heated than do the polymers with main inorganic molecular chains.

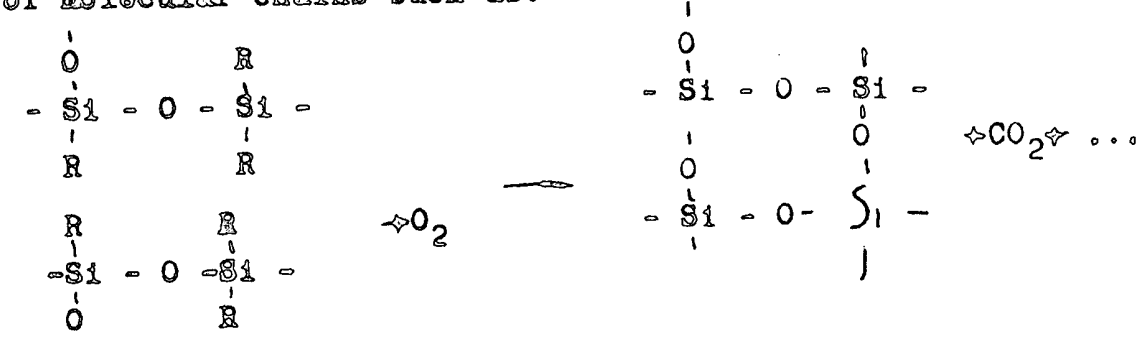
Polymers with inorganic molecular chains undergo considerable loss in weight only at the start of heating, then the process is strongly slowed down. On the other hand, the destruction of organic polymers proceeds continuously with volatile products being evolved at approximately the same rate.

Thermal oxidation destruction results in ready degradation of organic polymers, thermal oxidation reactions taking

thereby place not only in the groups fringing the main molecular chain but in the main chain as well. Destruction is accompanied by the formation of readily volatile oxidation products and in the extreme case that is, when exposed for a long time to heat and atmospheric oxygen, the polymer can be fully oxidised. Such instances occur in practice when polymers are applied as dielectrics in machines and apparatus in the form of thin films to be used for a long time under normal atmospheric conditions at 130° and above.

With polymers involving main inorganic molecular chains, carbon that gives rise on destruction to volatile oxygen containing compounds is not included in the main chain of the polymer molecule, participating only in the groups fringing the main chain. The main chains of these polymers are composed of elements that, contrary to carbon, on thermal oxidation destruction do not give rise to volatile compounds containing oxygen. Moreover, the main chains include also oxygen that brings about some oxidation of the element forming the main chain.

During thermal oxidation destruction the reactions take place essentially in the organic part of the molecule with the organic groups being oxidised and the polymer further structured to lead to oxidation being sterically hindered. Thus, thermal oxidation destruction results in the cross-linking of molecular chains such as:



the inorganic part of the molecule being thereby increased as seen from data listed in Table 2.

Of organic polymers under investigation only polytetrafluoroethylene is extremely stable to thermal oxidation as evidenced by its composition and molecular structure. This is primarily accounted for by the higher screening effect of fluarine fringing the main carbon chain of the molecule and by the good packing of molecular chains. When substituting chlorine for fluorine, say in polytrifluorochloroethylene, a sharp decrease in thermal oxidation stability is observed.

The study of the theremoplasticity of polymers investigated as films at 180, 200, 210, and 220° (see Table 3) also revealed a considerable difference in the properties of organic polymers and those involving chain inorganic molecular chains fringed with different organic groups. Films from organic polymers studied all were found to lose their elasticity on heating much more readily than did the films from main inorganic chains. Figure 2 shows the time of heating at various temperatures at which the films are elongated by less than 4 per cent. It will be seen that the dependence of thermoplasticity of different polymers on temperature is in fair agreement with Arrhenius' equation.

$$K = P z e^{-\frac{E}{RT}}$$

where K is the reaction rate constant, P the probability factor, z the number of collisions among the reacting molecules, E the activation energy, R the gas constant, and T the absolute temperature.

Calculating the activation energy E in terms of Arrhenius' equation for the polymer series the following values are obtained:

Polydimethylphenylsiloxane	36.0 kcal/mole
Polydimethylphenylsiloxane, modified	38.0 kcal/mole
Polyvinylformalethylal	26.7 kcal/mole
Polyester	25.7 kcal/mole

Thus, the activation energy of thermal oxidation destruction of polymers involving inorganic molecular chains as judged by thermo plasticity data is seen to be higher than that of organic polymers. It is to be noted that the values for activation energy in terms of thermoplascity are in rather close agreement with those obtained from the drop in the break down voltage on aging that proved to be in this case 33.0 kcal/mole for polydimethylphenylsiloxane and 24.8 kcal/mole for poly - ethyleneterephtalate.

The effect of the fringing group and the molecular chain structure of polymers with inorganic molecular chains on the change in weight is shown in Table 4. It will be seen that organic groups seriously affect the loss in weight of the polymer. Thus polymers with main chains fringed by ethyl groups lose more in weight than do the polymers involving phenyl and methyl groups. Only at temperatures above 400° do the polymers containing phenyl groups lose 52 per cent of their weight. This demonstrates that phenyl groups are readily split off only at temperatures above 400° whilst ethyl groups undergo ready oxydation at 250° and methyl groups at 300°.

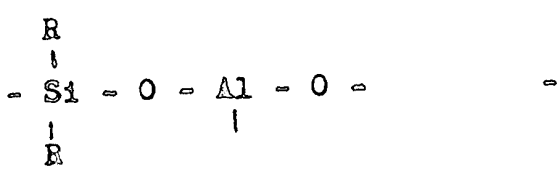
In Table 5 are given data showing the time needed for the

polymer to lose half of its organic groups. This is seen to vary considerably for different polymers.

Depending on the increasing stability to heating in the air of various fringing groups the polymers can be arranged in the following series

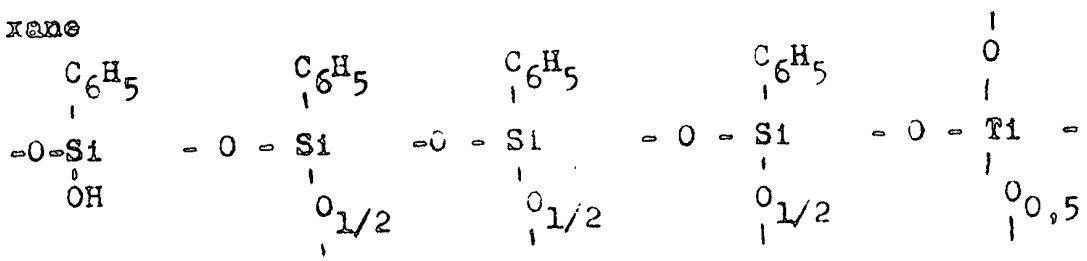
$$C_2H_5- \;<\; CH_3- \;<\; C_6H_5-$$

It is of interest to follow the changes in thermal oxidation stability of polymers involving inorganic molecular chains with the main molecular chain containing in addition to oxygen two elements. Tables 6 and 7 show the stability to thermal oxidation destruction of polymethylsiloxane containing units from

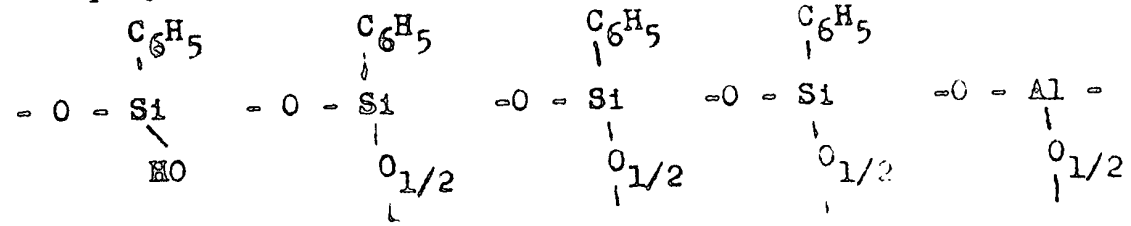


As seen from the Tables a considerable lowering of loss in weight on heating is observed but polymers containing aluminium substantially lose thereby their thermoplasticity.

The hydrolytic stability of polymers was exemplified by compounds of a general formula $\left[R_3SiO\right]_{-}M$ with M denoting aluminium, titanium, tin as well as by polytitanophenylsiloxane



and polyalumophenylsiloxane



The relative rate of hydrolysis has been found to depend on the particular metal forming part of the molecule

Table 9

Compound	Constants of rate of hydrolysis	Relative Rate of Hydrolysis
Sn /$OSi(C_2H_5)_3$/$_4$	200.10^{-3}	2220
Al/$OSi(C_2H_5)_3$/$_3$	$2.45.10^{-3}$	27.2
Ti/($OSi(C_2H_5)_3$/$_4$	$0.09.10^{-3}$	1

The investigation of the stability of polytitanophenylsiloxane to hydrolysis in acidic aqueous media showed that the Si - O - Ti bond does not readily hydrolyse. Figure 3 illustrated the hydrolytic cleavage of polytitanophenylsiloxane, polyalumophenylsiloxane, and polyalumoethyl siloxane with 10 and 30 per cent hydrochloric acid. Experiments have shown that under the action of 10 per cent hydrochloric acid the Si - O - -Ti bond in polytitanophenylsiloxane is broken only to a small degree, only 1.5 per cent of titanium having entered the solution in 10 hours. Under the same conditions the Si - O - Al bond in polyalumophenylsiloxane and polyalumoethylsiloxane underwent 87 and 68.7 per cent degradation, respectively. On the other hand 30 per cent hydrochloric acid had ruptured the Si - O - Ti bond in polytitanophenylsiloxane in 1 hour by 25 per cent. Under the same conditions the Si- O - Al bond in polyalumophenylsiloxane and polyalumoethylsiloxane was ruptured by 95.2 and 87.5 per cent, respectively. 30 per cent hydrochloric acid had ruptured the Si - O - Ti bond in polytitano-

phenylsiloxane by 40.8 per cent and Si - O - Al bond in polyalumophenyl- and polyalumoethyl-siloxanes by 100 per cent. Only when treated with 30 per cent hydrochloric acid for 10 hours did the Si - O - Ti bond in polytitanophenulsiloxane decompose by 50 per cent.

The quantitative evidence on the hydrolytic stability of polytitanophenylsiloxane, polyalumophenylsiloxane, and polyalumosiloxane were substantiated by chenical analysis of the products obtained after the hydrolysis of these polymers (see Tables 10 and 11). The results obtained suggest that the hydrolytic stability of the Si - O - Ti bond in polytitanophenylsiloxane is considerably higher than that of Si - O - Al in polyalumoorganosiloxanes.

Experimental

The thermal oxidation destruction was estimated by the loss in weight of the samples heated as powders (Table 1,4,6) and by the change in weight of pure films 0.05 mm thick and 50 x 100 mm in size.

The thermoelasticity of films on copper and aluminium supports was determined. The film was considered as having lost its elasticity when after being heated it gave cracks on bending at room temperature around a rod 3 mm in diameter.

Hydrolytic cleavage of polytitanophenylsiloxane with hydrochloric acid. Into a three necked flask equipped with a stirrer, thermometer and reflux, hzdrochloric acid of suitable concentration was poured, heated up to 95° and finely powdered polytitanophenylsiloxane was introduced. The polymer to

hydrochloric acid concentration was 1 to 1oo. The reaction was run for 1o hours, samples to be analysed being taken in 13,5,and 1o hours. Titanium content in its hydrochloric so - lutions was determined colorimetrically following the procedure described in the literature (3) with the results listed in Figure 3; a,b. The polymeric precipitate left after the reaction was removed from its hydrochloric solution, washed with water up to a negative chlorine test, dried at 1o5-11o° to constant weight and its elementary composition determined. The analytical data for the starting polytitanophenylsiloxane and the products of its hydrolytic cleavage are listed in Table 1o.

Table 1o

Polytitanophenyl siloxane	Elementary composition				Ratio of the number of silicon to titanium atoms in polymer
	C	H	Si	Ti	
Starting compound	48.52	4.58	16.8o	7.21	4.o
After hydrolytic cleavage with 1o% hydrochloric acid	46.95	3.98	18.24	7.6o	4.1
The same with 3o% hydrochloric acid	51.86	3.99	21.17	3.34	1o.8

Hydrolytic cleavage of polyalumophenyl siloxanes with aqueous solution of 1o and 3o per cent hydrochloric acid. This cleavage was carried out as above with the data given in Figure 3. The precipitates left after hydrolysis were carefully washed, dried, and analysed, the experimental data obtained being listed in Table 11.

Conclusions

1. The thermal oxidation stability of polymers involving main inorganic molecular chains consisting of silicon atoms, oxygen, and aluminium is higher than that of organic polymers. The destructive processes proceed in organic polymers at high temperatures to form volatile products followed by complete decomposition of molecules. With polymers containing main inorganic molecular chains these processes take place only in the organic part of the molecule and are accompanied by the structuring of the polymer that results in increased inorganic part of the polymeric molecule.

2. The thermal oxidation stability of polymers with main inorganic molecular chains is affected to a great extent by organic groups fringing the main chain.

3. The introduction into the main polymeric chain of aluminium together with silicon results in the increase in the thermal oxidation stability of the polymer.

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Table 1

Thermostability of polymers to thermooxydation destruction (decomposition)

Polymer	Chemical Composition	Loss in weight in 24 hr (%) at °C				
		250	300	350	400	450
Polydimethyl-phenylsiloxane	$-\left[\begin{matrix} CH_3 \\ Si \\ CH_3 \end{matrix} - O - \begin{matrix} C_6H_5 \\ SiO \\ O \end{matrix}\right]_x$	7.2	12.0	22.8	36.0	44.7
Polydiethyl phenyl siloxane	$-\left[\begin{matrix} C_2H_5 \\ Si \\ C_2H_5 \end{matrix} - O - \begin{matrix} C_6H_5 \\ SiO \\ O \end{matrix}\right]_x$	8.3	-	30.2	38.0	-
Polydimethylphenyl alumosiloxane	$-\left[\begin{matrix} CH_3 \\ SiO \\ CH_3 \end{matrix} - \begin{matrix} C_6H_5 \\ SiO \\ O \end{matrix}\right]_x \left[\begin{matrix} O \\ AlO \\ \end{matrix} - \begin{matrix} R \\ SiO \\ R \end{matrix}\right]_y$	-	5.0	8.8	13.0	-
Polytrifluoro-chloroethylene	$-\left[\begin{matrix} F \\ C \\ F \end{matrix} - \begin{matrix} F \\ C \\ F \end{matrix} -\right]_x$	1.3	-	2.1	2.5	45.7
Polytrifluoro chloroethylene	$\left[- \begin{matrix} Cl \\ C \\ F \end{matrix} - \begin{matrix} F \\ C \\ F \end{matrix} -\right]_x$	4.6	-	98.9	-	-
Polyamide (caprone)	$\left[\begin{matrix} O \\ \| \\ C(CH_2)_4 \end{matrix} \begin{matrix} O \\ \| \\ C-NH- \end{matrix}\right]_x$	55.5	-	94.3	-	-
Epoxydiphenyl propane	$-\left[O - C_6H_4 - \begin{matrix} CH_3 \\ C \\ CH_3 \end{matrix} - C_6H_4 - OCH_2CH_2O\right]_x$	22.7	-	93.1	-	-
Maleioglycol-polyester	$\left[-OCH_2CH_2OCOCH=CHOCO-\right]_x$	20.5	-	88.7	-	-
Polyethylene terphtalato	$-\left[OCH_2CH_2OC - C_6H_4 - \begin{matrix} O \\ \| \\ C- \end{matrix}\right]_x$	7.5	-	91.2	-	-
Phenol formaldehyde	$\left[C_6H_3(OH) - CH_2 - \right]_x$	5.3	-	68.0	-	-
Nitrile rubber	$-\left[CH_2 - \begin{matrix} CH_2- \\ \\ CN \end{matrix}\right]_x$	9.38	-	72.0		

Table 2

Changes in the elementary composition of polymers after thermal destruction

Condition for destruction	loss in weight	% C	% Si	C/Si
Polymethylsiloxane containing C, 17.8; Si, 40.9 %				
24 hr at 250°	2.76	17.12	40.73	1.07
2 hr at 350°	6.02	8.67	42.68	0.47
Polyphenylsiloxane containing C, 55.8; Si, 21.7 %				
24 hr at 450°	52.0	3.7	40.8	
6 hr at 550°	57.5	0.33	46.32	
Polydimethylsiloxane containing C, 32.7; Si, 38.0 %				
5 hr at 300°	29.5	28.86	38.78	1.74
5 hr at 350°	35.0	5.89	42.05	0.32

Table 3

Thermoelasticity of polymeric films

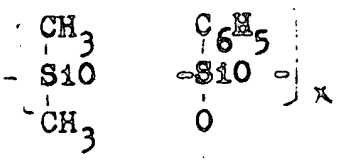
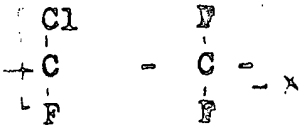
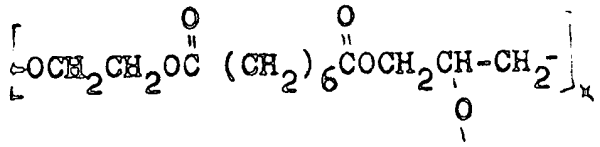
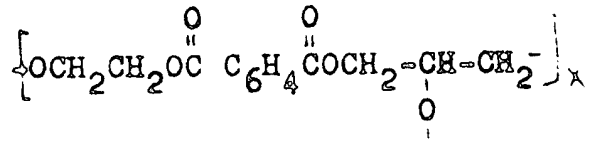
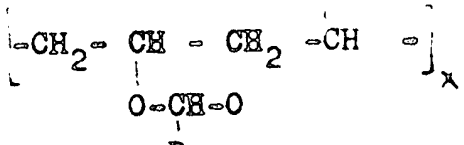
Polymer	Chemical composition	Thermoelasticity (hr, at °C)		
		180	200	210
Polydimethylpoly-phenylsiloxane		2000	700	150
Polytrifluorochloro ethylene		120	70	30
Glycol cebacynic glycerine polyester		20	6	0
Glycolterephtalic glycerine polyester		80	48	4
Polyvinylformal ethylal	 modified by rezole*	8	2	0
Epoxypolyester		32	28	-

Table 4

The effect of fringing groups on the thermooxydising stability of polymers

Polymer	Chemical composition	Loss in weight in 24 hr (%, at °C)				
		250	300	350	400	450
Polymethyl siloxane	$\left[\begin{array}{c} CH_3 \\ \vert \\ Si - O \\ \vert \\ O \end{array}\right]_x$	2.8	-	7.0	-	13.0
Polyphenyl siloxane	$\left[\begin{array}{c} C_6H_5 \\ \vert \\ Si - O \\ \vert \\ O \end{array}\right]_x$	2.0	-	3.0	8.5	51.5
Polydimethyl phenylsiloxane	$\begin{array}{c} CH_3 \\ \vert \\ Si \\ \vert \\ CH_3 \end{array} - O - \left[\begin{array}{c} C_6H_5 \\ \vert \\ Si - O \\ \vert \\ O \end{array}\right]_x$	7.2	12.0	22.8	36.0	44.7
Polydimethyl siloxane	$\left[\begin{array}{c} CH_3 \\ \vert \\ Si - O \\ \vert \\ CH_3 \end{array}\right]_x$	4.0	-	34.0	-	-
Polydiethyl phenylsiloxane	$\begin{array}{c} C_2H_5 \\ \vert \\ Si \\ \vert \\ C_2H_5 \end{array} - O - \left[\begin{array}{c} C_6H_5 \\ \vert \\ Si - O \\ \vert \\ O \end{array}\right]_x$	8.3	-	30.2	38.0	

Table 5

Polymer	Chemical composition	Temp. (°C)	The half life time (hr)
Polymethyl siloxane	$CH_3-Si-O-$ (O, x)	250	24
		350	2.0
		450	0.8
Polyethyl siloxane	C_2H_5 $-Si-O-$ (O, x)	250	0.8
		350	0.7
		450	0.5
Polyphenyl siloxane	C_6H_5 $-Si-O-$ (O, x)	350	24
		400	10
		450	3.2
		550	0.8
Polydimethyl phenylalumo siloxane	CH_3 C_6H_5 $-Si-O-Si-O-$ (CH_3, O, x)	350	12
		400	5
Polydimethyl phenylalumo siloxane	CH_3 C_6H_5 $Si-O-Si-O-Si-O-Al-$ (CH_3, O, O, x)	350	20
		400	10

Table 6

Loss in weight of the polymer (%)

Polymer	Chemical composition	Time (hr)	Heating (hr, at °C)				
			200	250	300	350	400
Polydiethyl polyphenyl siloxane	$\left[\begin{array}{c} C_2H_5 \quad C_6H_5 \\ -Si-O-Si-O- \\ C_2H_5 \quad O \end{array}\right]_x$	24	10.0	16.0	20.5		
		72	13.5	28.0	33.0		
		360	21.0	30.0	45.0		
Polydimethyl polyphenyl siloxane	$\left[\begin{array}{c} CH_3 \quad C_6H_5 \\ -Si-O-Si-O- \\ CH_3 \quad O \end{array}\right]_x$	24	3.0	4.5	12.0		
		72	3.75	5.8	17.2		
		360	4.5	6.3	22.0		
Polydimethyl polyphenyl aluminosiloxane	$\left[\begin{array}{c} CH_3 \quad C_6H_5 \\ -Si-O-Si-O- \\ CH_3 \quad O \end{array}\right]_x \left[\begin{array}{c} R \\ -SiO-AlO- \\ R \quad O \end{array}\right]_y$	24	-	-	5.0	8.8	13.0
		72	-	-	8.4	12.0	18.0
		360	-	-	10.0	15.0	29.0

Table 8

Thermoelasticity of polymeric films

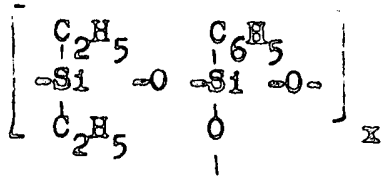
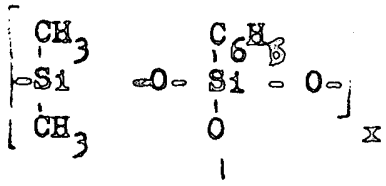
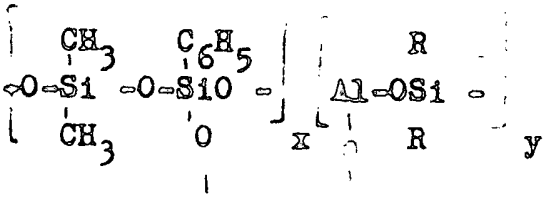
Polymer	Chemical composition	Thermoelasticity (hr, at °C)		
		180	200	220
Polydiethyl polyphenyl siloxane		-	90	18
Polydimethyl polyphenyl siloxane		-	700	150
Polydimethyl polyphenyl alumosiloxane		-	48	24

Table 11

Polyalumophenyl siloxane	Elementary composition (%)				Ratio of the number of silicon to aluminium atoms in the polymer
	C	H	Si	Al	
Starting compound	49.58	3.54	17.7	4.31	3.96
After hydrolytic cleavage with 10% hydrochloric acid	51.61	4.16	20.11	0.79	24.20
The same with 30% hydrochloric acid	52.96	4.02	19.33	traces	

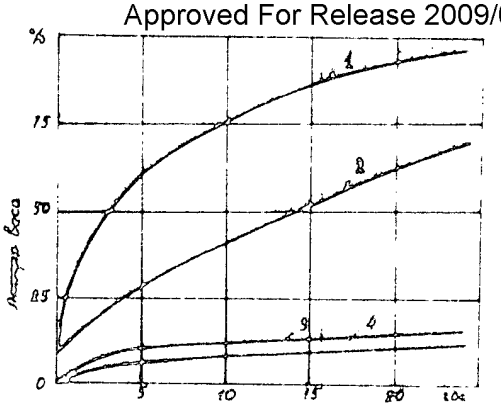
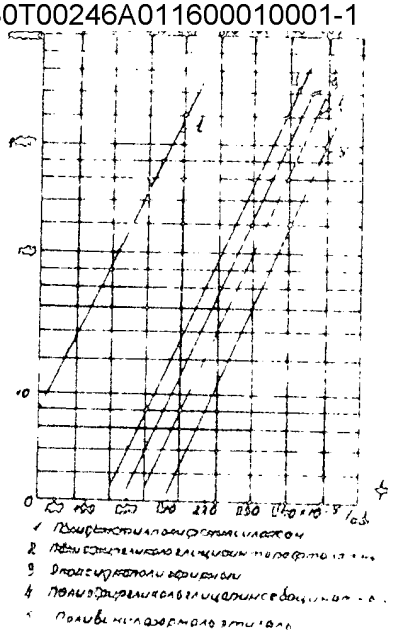


Рис 1 Кинетика деструкции полимеров при температуре 350°С

1 - винипласт, 2 - фенолформальдегидной смолы, 3 - полиметилсилоксан, 4 - полиимид



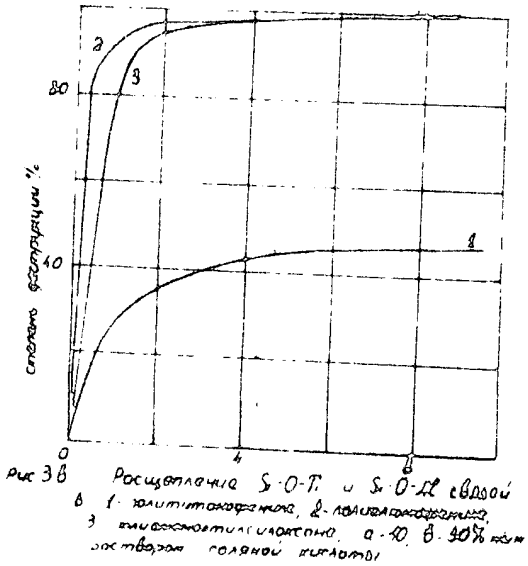


Рис 3 в Расщепление S-O-T и S-O-C связей в 1 - политетрафторэтилене, 2 - полиэтилентерефталате, 3 - полиметилсилоксане, а - 10, в - 90% водных растворах серной кислоты

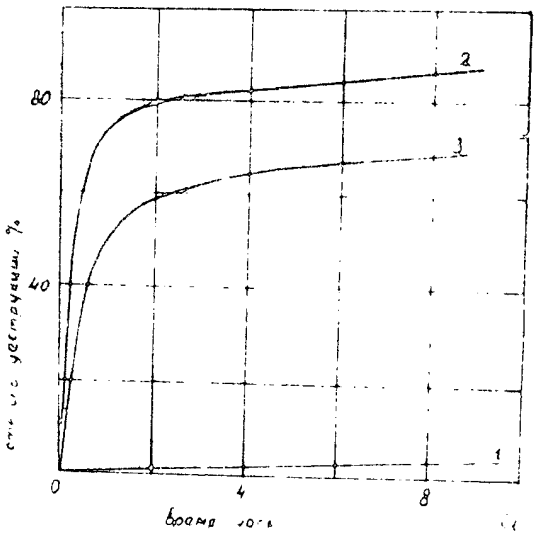
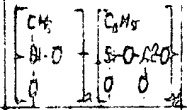
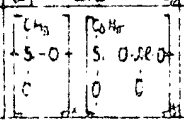


Таблица 7

Название полимера	Химический состав	До прогрева	После прогрева при 450° в течение 5 час	
		содержание углерода в %	содержание углерода в %	остаток веса в %
Полиметилсилоксан	$(CH_3SiO_{1,5})_x$	18,90	4,2	98,6
Полиэтилентерефталат		80,1	13,92	8,12
Полиметилфенилсилоксан		84,1	14,2	91,1